

Specification

CARPET, STAINPROOFING AGENT FOR CARPET
AND METHOD FOR TREATING THE CARPET

Field of the Invention

5 The invention relates to a stainproofing agent
for carpet, a method for stainproofing a carpet and
stainproof-treated carpet.

Background Art

 A variety of stainproofing agents are proposed
10 to impart water-repellency, oil-repellency and stainproof
properties to textile (eg. carpet).

 Japanese Examined Patent Publication No.
8606/1973 discloses that stainproof properties are
imparted by treating fibers with a homopolymer obtained
15 by polymerizing an ester of an unsaturated carboxylic
acid having a perfluoroalkyl group at both ends.
However, this homopolymer is insufficient in stainproof
properties.

 Japanese Examined Patent Publication No.
20 3767/1976 discloses that stainproof properties are
imparted to fibers by treating the fibers with a polymer
obtained by polymerizing (i) an ester of maleic or

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fumaric acid having a perfluoroalkyl group at one end and an aliphatic or aromatic group having no fluorine atom at the other end with (ii) the other polymerizable unsaturated compound. Since one end of the ester of maleic or fumaric acid has no fluorine atom, its polymerizablity is good. However, this polymer is insufficient in water- and oil-repellency and is also insufficient in stainproof properties.

U.S. Pat. No. 3,594,353 discloses that a water repellency and stainproof properties to oil are imparted to fibers by treating the fibers with a polymer obtained by homopolymerizing an ester of itaconic acid having a perfluoroalkyl group at both ends or one end or copolymerizing said ester with the other polymerizable unsaturated compound. However, this polymer is insufficient in water- and oil-repellency and stainproof properties.

None of stainproofing agents which have hitherto been proposed presently has sufficient water- and oil-repellency, stainproof properties and also cleaning durability.

Although a carpet treated by a conventional

method to impart water-repellency, oil-repellency and stainproof properties thereto is better than untreated carpet in initial water-repellency, oil-repellency and stainproof properties, the properties are insufficient, and cleaning durability of the carpet is also insufficient.

It is an object of the invention to provide a carpet with excellent initial water-repellency and stainproof properties and also outstanding cleaning durability, a stainproofing agent for carpet, a method for stainproof treatment of carpet.

Disclosure of the invention

The inventors conducted extensive research to solve such problems and found that excellent water-repellency, stainproof properties and cleaning durability may be imparted to a carpet by treating the carpet with a stainproofing agent and a specific crosslinking agent, thus the invention has been accomplished.

Thus, the invention relates to a carpet to which stainproof properties and cleaning durability are imparted by treating the carpet with (i) a fluoroalkyl-containing compound and (ii) a triazine ring-containing

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crosslinking agent, a stainproofing agent and
a method for stainproof treatment of a carpet.

Stainproof degree of carpet of the invention
maintains at least 30 % after cleaning of 3 times,
5 preferably 5 times, more preferably 10 times, further
preferably 15 times, in particular 20 times.

The fluorine-containing stainproofing agent
comprising a fluoroalkyl group (hereinafter referred to
as "Rf") containing compound is not specifically limited
10 to, but includes known compounds.

Examples of the fluorine-containing
stainproofing agent comprising Rf group-containing
compound are:

UNIDYNE TG-3010, TG-3020, TG-3040, TG-3510, TG-3520, TG-
15 3710, TG-3720, TG-3711, TG-452, TG-452A, TG-930, TG-232
(DAIKIN Industries Ltd.);

SCOTCHGUARD FX-1367F, FX-1373M, FX-1355, FC-393, FC-367,
FC-369, FC-398, FC-399 (Minnesota Mining and
Manufacturing Co.);

20 ZONYL FCC, 8779, AFC, NRD-372, N-140, N-119 (E.I. du Pont
de Nemours and Company);

ASAHIGUARD AG-820, AG-850, AG-923 (ASAHI GLASS CO.,

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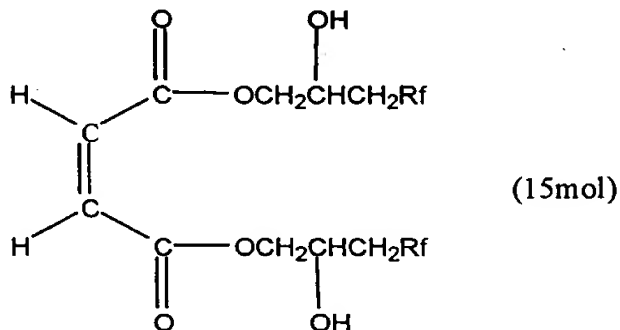
LTD.);

NUVA-FT, FTA (HOECHST AG); and

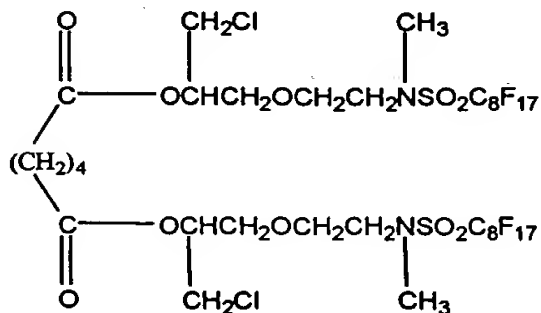
CRS-7 (NIKKA KAGAKU).

Specifically, the fluorine-containing stainproofing agent includes fluoroalkyl-containing maleic acid diester copolymer, fluoroalkyl-containing adipic acid diester compound and fluoroalkyl-containing urethane compound as shown below.

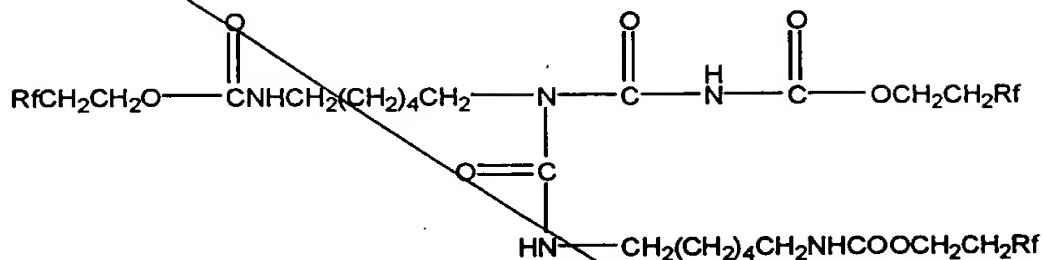
(1) Fluoroalkyl-containing maleic acid diester copolymer



(2) Fluoroalkyl-containing adipic acid diester compound



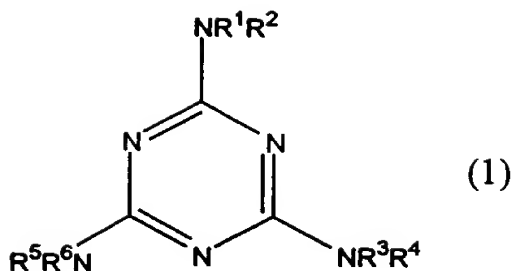
(3) Fluoroalkyl-containing urethane compound



wherein Rf represents $\text{C}_n\text{H}_{2n+1}$ (n is an integer of 5 to 21).

The amount of fluorine atom in solid content of stainproofing agent preferably ranges from 50 to 10,000 ppm based on the unit weight of carpet pile. Less than 50 ppm of the amount of fluorine atom results in insufficient stainproof properties. More than 10,000 of the amount of fluorine atom does not greatly improve stainproof properties.

The triazine ring-containing compound of the invention represented by formula (1) improves an adhesion property between said fluorine-containing stainproofing agent comprising Rf-containing compound and carpet pile, and also hardens coating:



wherein R¹ to R⁶ are the same or different, and represent -H, -OH, -CH₂OCH₃, -CH₂OH, -CH₂CH₂OH, -CH₂CH₂CH₂OH, or -CH₂OC₂H₅, preferably -CH₂OH.

As crosslinking agent represented by formula
5 (1), trimethylolmelamine and hexamethylolmelamine are particularly preferable. Example of commercial name of the crosslinking agent is SUMITEX RESIN M-3 (trimethylolmelamine; SUMITOMO CHEMICAL Co. LTD.).

Coating mass of the triazine ring-containing
10 compound preferably ranges from 0.01 to 1.0 % by weight based on the unit weight of carpet. When coating mass is less than 0.01 % by weight, cleaning durability is insufficient. When coating mass is more than 1.0 % by weight, cleaning durability is not improved but results

Catalyst is preferably added to the triazine ring-containing compound to accelerate a reaction.

like organic carboxylic acids; organic carboxylates

hydrochloric acid, phosphoric acid, nitric acid and like
inorganic acids; inorganic acid salts between the

magnesium, zinc, aluminum, iron, etc. The amount of catalyst is not specifically limited to, but usually 100 % by weight based on the amount of triazine ring containing compound.

The stainproofing agent for carpet may be in the form of aqueous dispersion or solution in a solvent.

The stainproofing agent of the present invention can be applied by any method according to the kind of the material to be treated. For example, there can be used a method for applying the agent of the invention on the surface of material to be treated, using a known application procedure such as immersion, coating,

etc., followed by drying. Furthermore, the stainproofing agent of the present invention may further comprise additives and a crosslinking agent other than said crosslinking agent. For example, polymethyl methacrylate
5 /ethyl methacrylate (P-MMA/EMA) and like polymer, additives such as insect repellents, flame retardants, antistatic agents, dye fixing agents, wrinkle inhibitors, softeners and stain block agents which inhibit adhesion of acid dye may be appropriately added.

10 The material to be treated with the stainproofing agent of the present invention is preferably a textile, in particular, a carpet. Examples of the textile are animal-origin natural fibers such as cotton, hemp, wool, silk, etc.; synthetic fibers
15 such as polyamide (nylon), polyester, polyvinyl alcohol, polyacrylonitrile, polyvinyl chloride, polypropylene, etc.; semisynthetic fibers such as rayon, cellulose acetate, etc.; inorganic fibers such as glass fibers, carbon fibers, asbestos fibers, etc.; and a mixture of
20 these fibers. Preferable fibers are polyamide (nylon), polyester, polyvinyl alcohol, polyacrylonitrile, polyvinyl chloride, polypropylene and like synthetic

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fibers, rayon, cellulose acetate and like semisynthetic fibers or a mixture thereof. The textile may be in any form such as a fiber, a yarn, a cloth and the like. When a carpet is treated with the stainproofing agent of the present invention, the carpet may be formed after treating fibers or yarns with the stainproofing agent. Alternatively, the formed carpet may be treated with the stainproofing agent.

The carpet of the invention may be pre-treated with stain block agent before stainproof treatment. Examples of stain block agent are generally a poly(meth)acrylic acid and a sulphonic acid-containing phenol/formaldehyde condensation product, specifically FX-668F (Minnesota Mining and Manufacturing Co.), SR-300 (E.I. du Pont de Nemours and Company). The stain block agent is preferably used in a sufficient amount which allow 0.05-10 % by weight of active ingredient based on the weight of carpet to be adhered on carpet. Stain block agent may be applied according to a usual treatment process such as hot air treatment, steam treatment, boiled water treatment, etc.

The stainproofing agent of the invention may

further comprises PEG and/or a copolymer comprising
(1) at least one selected from polyoxyethylene chain-
containing acrylate and methacrylate; and
(2) at least one reactive monomer selected from glycerol
5 methacrylate and glycidyl methacrylate).

The copolymer or PEG may be used in an amount
of 1-50% by weight, preferably 2-20% by weight based on
the solid content of repellant.

Color of carpet to be treated includes blue.

10 With respect to color of carpet,

L = 40 to 80, preferably L = 40 to 60;

a = +0.1 to -0.8, preferably a = -0.1 to -0.6;

b = -13 to -25, preferably b = -17 to -21.

The carpet of the invention maintains a
15 stainproof degree during resoiling of at least 20%,
preferably at least 30% after one cycle of contamination,
cleaning and recontamination.

Best Mode for Carrying out the Invention

The invention is described below in detail by
20 way of example. However, the invention is in no way
limited to the examples.

Evaluation procedures of water-repellency, oil-

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repellency and stainproof property, and cleaning process are shown below.

<Water-repellency>

Five drops of isopropanol/water mixture having the following composition are slowly placed on the surface of carpet textile. Water repellency is represented by a maximum score at which at least 4 drops maintain a liquid form (repellent) after 3 minutes.

Table 1

Score	Composition (% by volume)	
	Isopropanol	Water
0	0	100
2	2	98
5	5	95
10	10	90
15	15	85
20	20	80
25	25	75
30	30	70
40	40	60
50	50	50

<Oil-repellency>

According to AATCC-TM-118-1966, five drops of the following test solution are slowly placed on the surface of carpet. Penetration state of the drops are observed after 3 minutes. Oil-repellency is represented by a maximum score at which at least 4 drops show no penetration into carpet.

Table 2

Score	Test solution	Surface tension (mN/m; 25°C)
0	Inferior to 1	
5	1 Nujol	31.2
	2 A mixture of N-hexadecane(35 parts by weight) and Nujol (65 parts by weight)	29.6
	3 n-hexadecane	27.3
10	4 n-tetradecane	26.7

<Stainproof property test 1>

Carpet treated with a stainproofing agent is evaluated according to AATCC-123-1995.

Carpet textile is cut into a 5.5cm x 8cm test piece. The test piece is allowed to stand in thermohygrostat (21°C, 65%RH) for 4 hours, dried sufficiently, followed by contaminated with a dry soil having the following composition. Specifically, five carpet test pieces are attached to a ball mill in such a manner that the stainproof surface of the carpet is in an upward direction. 0.031 g of dry soil per 1cm² surface area of the carpet test piece (corresponding to 6.82g in case of five carpet test pieces) and 50 ceramic balls (2.0 cm in diameter) are put in the ball mill. The ball mill is then rotated at 80 rpm for 7.5 minutes to give the carpet test piece on the surface of which the dry

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soil is uniformly adhered. The ball mill has a tubular shape, and a base inner diameter of 12.0 cm and a height of 9.5 cm. The excessive dry soil on the carpet test piece is thoroughly removed by aspiration with domestic

5 vacuum cleaner. Color difference (ΔE) on the surface of carpet is determined with color difference meter (MINOLTA CR-310). Stainproof ratio (%) is calculated on the basis of the following equation.

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$$\text{Stainproof ratio (\%)} = 100 \times (\Delta E_N - \Delta E_{Tn}) / \Delta E_N$$

10 ΔE_N : Color difference after stainproof test of untreated carpet

ΔE_{Tn} : Color difference after stainproof test of carpet treated by the stainproofing agent

n : the number of cleaning

Composition	Content (% by weight)
1. Polyethylene Glycol (PEG) 400	60.0
2. Propylene Glycol	30.0
3. Glycerol	10.0
4. Water	0.0
5. Sodium Chloride	0.5
6. Potassium Chloride	0.5
7. Calcium Chloride	0.5
8. Magnesium Chloride	0.5
9. Zinc Chloride	0.5
10. Iron Chloride	0.5
11. Copper Chloride	0.5
12. Nickel Chloride	0.5
13. Cobalt Chloride	0.5
14. Manganese Chloride	0.5
15. Barium Chloride	0.5
16. Strontium Chloride	0.5
17. Lead Chloride	0.5
18. Bismuth Chloride	0.5
19. Antimony Chloride	0.5
20. Arsenic Chloride	0.5
21. Vanadium Chloride	0.5
22. Chromium Chloride	0.5
23. Molybdenum Chloride	0.5
24. Tungsten Chloride	0.5
25. Uranium Chloride	0.5
26. Thorium Chloride	0.5
27. Radium Chloride	0.5
28. Actinium Chloride	0.5
29. Protactinium Chloride	0.5
30. Neptunium Chloride	0.5
31. Plutonium Chloride	0.5
32. Americium Chloride	0.5
33. Curium Chloride	0.5
34. Berkelium Chloride	0.5
35. Californium Chloride	0.5
36. Einsteinium Chloride	0.5
37. Fermium Chloride	0.5
38. Mendelevium Chloride	0.5
39. Nobelium Chloride	0.5
40. Lawrencium Chloride	0.5
41. Rutherfordium Chloride	0.5
42. Dubnium Chloride	0.5
43. Seaborgium Chloride	0.5
44. Bohrium Chloride	0.5
45. Hassium Chloride	0.5
46. Meitnerium Chloride	0.5
47. Darmstadtium Chloride	0.5
48. Roentgenium Chloride	0.5
49. Copernicium Chloride	0.5
50. Nihonium Chloride	0.5
51. Flerovium Chloride	0.5
52. Livermorium Chloride	0.5
53. Tennessine Chloride	0.5
54. Oganesson Chloride	0.5

5	Kaoline	18
	Silica	18
	Carbon black	1.15
	Iron oxide	0.3
	<u>Nujol</u>	<u>6.25</u>

10 with respect to Lab values, L : 25-31, a : 2.3-2.6, b :
4.2-4.8.

15 <Stainproof property test 2> is evaluated in the same manner as <Stainproof property test 1> except that the size of carpet textile is 11cm x 8cm; and that the amount of dry soil per 1cm² surface area of the carpet test piece is 0.0062g (corresponding to 1.64g in case of three carpet test pieces); and that rotation conditions are 80 rpm for 5 min.

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~~Cleaning of the carpet textile treated with a~~

~~Stainproofing agent is conducted according to AARCC-138.~~

Stated more specifically:

- (i) the surface of carpet test piece (11cm x 11cm) is washed with running water (50°C) for 1 min, followed by squeezed with mangle (pressure : 5mg/cm²).
- (ii) The carpet test piece is fixed and set on the testing stand of cleaning test machine (STAIN & CLEANING TESTER: YOSHIDA SEIKI SEISAKUSYO) as defined in JIS L1023-1992 in order that rotary brushes rub carpet piles.
- (iii) Cleaning of the carpet is carried out by pouring 4.1ml of 1 % sodium lauryl sulfate (SLS) aqueous solution (adjusted at pH 8 with NaOH aqueous solution) warmed to 50°C to carpet with pipette, followed by rotating rotary brush and testing stand.
- One cleaning is composed of 5 rotations in regular direction, 5 rotations in reverse direction, further 5 rotations in regular direction and 5 rotations in reverse direction during which rotary brushes maintain rubbing carpet.
- "Cleaning three times" mean that the process is repeated 3 times except that SLS 1% aqueous solution is not further added.

"Cleaning five times" means that the process is repeated 5 times except that SLS 1% aqueous solution is not added.

The number of revolutions of the testing stand is 20 rpm. The number of rotation of brush is 240 rpm. Vacuum and water jet nozzle of cleaning test machine are not used.

The carpet is thoroughly rinsed with running water (50°C), squeezed with mangle, and then dried in hot-air drying chamber at 105°C for 30 min leading to completion of cleaning.

Example 1

Nylon 6,6 carpet textile (cut pile, pile density: 40 oz/yd², pile height: 1/4 inch, color: light blue) was dipped in water, squeezed with mangle to adjust wet pickup (the increased weight, represented by % by weight, of carpet after dipping in comparison with initial weight of carpet test piece) at 20% by weight.

A Stainproofing agent composition as shown in table 4 was prepared by mixing and stirring 8 parts by weight of UNIDYNE TG-3010 (Rf group-containing stainproofing agent for carpet; DAIKIN INDUSTRIES LTD.),

1.9 parts by weight of SUMITECH RESIN M-3

(trimethylolmelamine: SUMITOMO CHEMICAL CO., LTD.), 0.6

part by weight of SUMITECH ACCELERATOR (ACX; catalyst for SUMITECH RESIN M-3 which is a product of SUMITOMO

5 CHEMICAL CO., LTD.) and 89.5 parts by weight of water.

The carpet test piece (20g) was treated with the stainproofing agent composition (1.5g; corresponding to 400ppm fluorine atom per 1g of carpet), followed by heat-treated with pin stenter at 130°C for 10 min.

10 The carpet test piece was cleaned (1 time, 3 times, 5 times) according to the above-defined method to evaluate water-repellency, oil-repellency and stainproof property before and after cleaning. The results are shown in table 6.

15 Examples 2-6

 Stainproofing agent compositions as shown in table 4 were prepared. The carpet test piece was treated in the same manner as example 1.

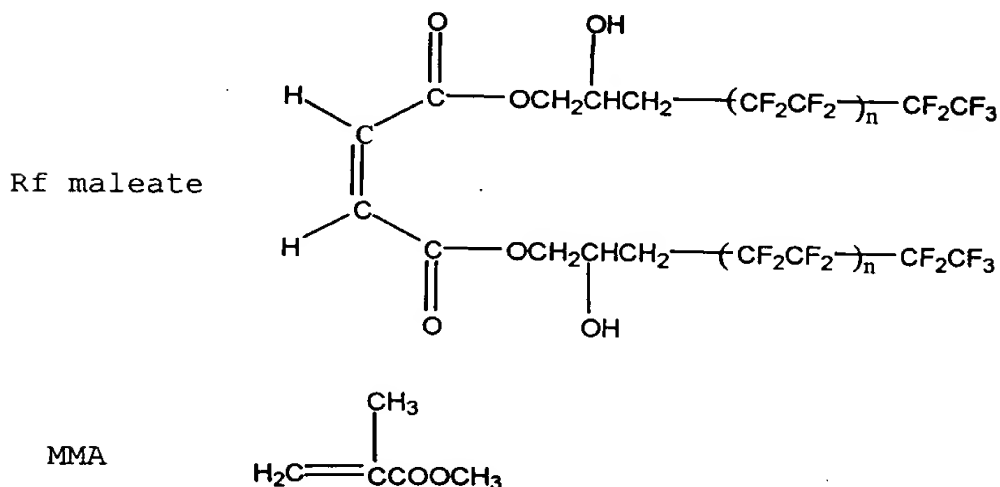
 The results are shown in table 6.

20 Example 7

 A stainproofing agent composition was prepared by diluting 6 parts by weight of emulsion (solid content

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30 % by weight) comprising Rf-maleate/methylmethacrylate (MMA)=60/40 (weight ratio) copolymer, SUMITEX RESIN M-3 and SUMITEX ACCELERATOR (ACX) with 94 parts by weight of water. The carpet test piece was treated with the stainproofing agent composition thus obtained in the same manner as example 1.



wherein n is an integer of 3 to 8.

Examples 8-10

The carpet test piece shown in example 1 was subjected to stain block processing. To a stain block agent (FX-668F: Minnesota Mining and Manufacturing Co.) diluted to 0.7% with water was added MgSO_4 (1%), and pH of the solution was adjusted at 2 with sulfamic acid.

The carpet test piece was boiled in the solution for 5 minutes. The test piece was washed with running water to remove an excess stain block agent and dried at 130°C. The resulting carpet test piece was dipped in water, 5 squeezed with mangle to adjust wet pickup thereof at 20%.

Stainproofing agents as shown in table 4 were prepared to treat the carpet test piece in the same manner as example 1. The results are shown in table 6.

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A stain block agent is a treatment applied to a 10 material in order to inhibit adhesion of acid dye in the process of stainproof processing of carpet.

Comparative examples 1-4

Stainproofing agent mixtures shown in table 5 were prepared and used for treating the carpet test piece 15 in the same manner as example 1. The results are shown in table 6.

Table 4

Ex.	Rf-containing Stainproofing Agent	Crosslinking Agent	Water (Wt.part)	Other Additives
5	Kind/Amount (Wt. Part)	Kind/Amount (Wt. Part)		Kind/Amount (Wt. Part)
	1 UNIDYNE	SUMITEX	89.5	ACX(0.6)
	TG3010/8	RESIN M-3/1.8		
	2 UNIDYNE	SUMITEX	89.8	ACX(0.3)
10	TG3010/8	RESIN M-3/0.9		
	3 Rf-maleate-MMA Copolymer 30% Emulsion/5	SUMITEX	93.8	ACX(0.3)
		RESIN M-3/0.9		
	4 SCOT GUARD	SUMITEX	93.8	ACX(0.3)
15	FX-1373M/5	RESIN M-3/0.9		
	5 SCOT GUARD	SUMITEX	89.2	ACX(0.7)
	FX-1367F/8	RESIN M-3/2.1		
	6 N-140/5	SUMITEX	93	ACX(0.5)
		RESIN M-3/1.5		
20	8 UNIDYNE	SUMITEX	89.8	ACX(0.3)
	TG3010/8	RESIN M-3/1.8		
	9 Rf-maleate-MMA Copolymer 30% Emulsion/5	SUMITEX	93.8	ACX(0.3)
		RESIN M-3/0.9		
25	10 SCOT GUARD	SUMITEX	89.2	ACX(0.7)
	FX-1367F/8	RESIN M-3/2.1		

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Table 5

Comp. Ex.	Rf-containing Stainproofing Agent	Crosslinking Agent	Water (Wt.part)	Other Additives
	Kind/Amount (Wt. Part)	Kind/Amount (Wt. Part)		Kind/Amount (Wt. Part)
5	1 UNIDYNE TG3010/8	- / -	89.5	-
10	2 Rf-maleate-MMA Copolymer 30% Emulsion/5	- / -	89.8	-
	3 Rf-maleate-MMA Copolymer 30% Emulsion/5	ELASTRON BN-69/1.5	93.35	Cat64 (0.15)
15	4 SCOT GUARD FX-1367F/5	- / -	93.8	-

Table 6

		Water-Repellency (Score)				Oil-Repellency (Score)				Stainproof Ratio (%)			
	Number of Cleaning	0	1	3	5	0	1	3	5	0	1	3	5
	Example 1	20	15	15	15	0	0	0	0	41	39	37	35
	Example 2	20	15	10	10	0	0	0	0	41	38	35	33
25	Example 3	20	20	15	15	0	0	0	0	42	40	38	35
	Example 4	20	20	15	15	0	0	0	0	40	39	38	36
	Example 5	25	25	25	20	1	1	1	1	50	49	47	43
	Example 6	25	20	20	15	0	0	0	0	52	50	48	45
	Example 7	20	15	15	10	0	0	0	0	40	38	37	32
30	Example 8	25	15	15	10	0	0	0	0	55	54	51	49
	Example 9	30	25	20	20	0	0	0	0	55	55	54	54
	Example 10	30	25	20	20	1	1	1	1	55	55	54	54
	Comp.Ex.1	20	0	x	x	0	0	0	0	43	28	18	15
	Comp.Ex.2	20	15	0	0	0	0	0	0	41	27	21	18
35	Comp.Ex.3	20	15	5	5	0	0	0	0	27	26	25	24
	Comp.Ex.4	10	5	x	x	1	1	1	0	33	28	22	15

In table 3, the number of cleaning "0" means

before cleaning.

With respect to stainproof ratio, carpet which is not treated with a stainproofing agent has a stainproof ratio of 100% before contamination and 0% after contamination.

Example 11

Stain block processing was carried out in advance in the same manner as examples 8-10.

A stainproofing agent composition was prepared by mixing 8 parts by weight of TG-3010, 0.9 part by weight of SUMITEX RESIN M-3, 0.3 part by weight of SUMITEX ACCELERATOR, 0.7 part by weight of polyethyleneglycolmethacrylate(PEGMA)/glycerol methacrylate(GMA)=70/30 (by weight ratio) copolymer and 90.1 parts by weight of water. The carpet test piece was treated by the composition in the same manner as example 1.

The test piece was subjected to a test cycle comprising <stainproof property 2>, cleaning and <stainproof property 2>. After the last <stainproof property 2> treatment, stainproof ratio of the test piece was determined. The results are shown in table 8.

Comparative example 5

Stain block processing was carried out in advance in the same manner as examples 8-10.

A stainproofing agent composition as shown in table 7 was prepared. The carpet test piece was treated with the stainproofing agent composition in the same manner as example 1. The test piece was subjected to the evaluation test as shown in example 11. The results are shown in table 8.

10

Table 7

	Rf- Containing Stain- proofing Agent	Cross- linking Agent	PEGMA/GMA Copolymer	Water (Wt.Part)	Other Additive
	Kind/Amount (Wt. Part)	Kind/Amount (Wt. Part)	(Wt. Part)		Kind/Amount (Wt. Part)
15	Ex.11 UNIDYNE TG3010/8	SUMITEX RESIN M-3/0.9	0.7	90.1	ACX(0.3)
20	Comp. UNIDYNE Ex.5 TG3010/8	- / -	- / -	92	- / -

Table 8

	<u>Stainproof ratio (%)</u>	
	<u>Initial</u>	<u>Recontamination</u>
25	Ex.11 65	35
	Comp. Ex.5 60	15

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